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Influence of ns-Nd:YAG laser surface treatment on the tensile bond strength of zirconia to resin-matrix cements

Bruno Henriques[a,b,c], Nathalia Hammes[a], Júlio C. M. Souza[a,d], Mutlu Özcan[e], Joana Mesquita-Guimarães[a], Filipe S. Silva[a], Márcio C. Fredel[b], Claudia M. Volpato[c], Óscar Carvalho[a]

[a]Center for MicroElectroMechanical Systems (CMEMS-UMinho), University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal

[b]Ceramic and Composite Materials Research Group (CERMAT), Federal University of Santa Catarina (UFSC), Campus Trindade, Florianópolis/SC, Brazil

[c]School of Dentistry (DODT), Postgraduate Program in Dentistry (PPGO), Federal University of Santa Catarina, Campus Trindade, 88040-900, Florianópolis/SC, Brazil

[d]School of Dentistry, University Institute of Health Sciences (IUCS), CESPU, Gandra PRD, Portugal

[e]Dental Materials Unit, Center for Dental and Oral Medicine, Clinic for Fixed and Removal Prosthodontics and Dental Materials Science, University of Zürich, Zürich, Switzerland.

Corresponding author:

Bruno Henriques (bruno.henriques@ufsc.br)

Óscar Carvalho (oscar.carvalho@gmail.com)

Abstract

The main aim of this study was to assess the effect of ns-Nd:YAG laser structuring over zirconia green compacts on the adhesion of sintered zirconia to resin-matrix cements. Zirconia (3Y-TZP) compacts were divided according to the type of surface modification: GB – alumina grit-blasted sintered specimens; G8L – laser structured zirconia green compacts (square pattern 8 lines); G16L - laser structured zirconia green compacts (square pattern 16 lines); G8L/GB – alumina grit-blasted G8L specimens after sintering. Specimens of same group were cleaned, cemented using a dual cure resin-matrix cement and aged in distilled water for 24 h (37ºC). Afterwards, the tensile bond strength was measured using a universal test machine. Specimens were analyzed by field emission guns scanning electron microscopy (FEGSEM) and white light interferometry (WLI). Laser-structured surfaces showed higher roughness values and improved morphological aspects for adhesion to resin-matrix cements. Higher tensile bond strength mean values of zirconia to resin-matrix cements were recorded for G8L (16.7 ±3.8 MPa) and G16L (13.6 ±3.0 MPa) groups when compared to those recorded for ordinary grit-blasted zirconia surfaces to resin-matrix cements (10 ±3.1 MPa). The highest tensile bond strength results were recorded for the G8L/GB group (24.2 ±7.6 MPa). The laser texturing of green zirconia surfaces promoted an increase in roughness and changes in morphological aspects of sintered zirconia for improved adhesion to resin-matrix cements.

Keywords: zirconia; resin cement; adhesion; green compacts; laser structuring; tensile bond strength

1. Introduction

Recent advances in restorative dentistry has been based in the development of novel ceramic materials with increasingly attractive optical and physical properties. In this way, zirconia has been the first choice for all-ceramic single-unit frameworks and highly aesthetic monolithic zirconia restorations with adequate color and translucency that mimic tooth structures [1]. Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) is therefore a material characterized by its high chemical stability and biocompability, mechanical strength (>1000 MPa of flexural strength), fracture toughness (~10 $MPa.m^{1/2}$), and aesthetics [1–3]. The high chemical stability itself can be seen as an advantage when it comes to the unleashing of undesired degradation products in the human body. However, the chemical stability of sintered zirconia becomes a challenge for surface modification and establishment of adhesion to veneer porcelain or to resin-matrix cements. Dental cements have been used in restorative dentistry as a luting agent to fill the space between a restoration fabricated outside the mouth and the tooth or implant structure. By flowing into irregularities in both materials and then hardening, the cement provides mechanical retention [4]. Etching with hydrofluoric acid is successfully used for surface modification (create irregularities) of lithium disilicate-reinforced glass-ceramics and feldspar-based porcelains although there is no effect on zirconia-based surfaces in which the glassy phase is absent [5,6]. Additionally, the lack of silica (SiO_2) on its composition also prevents the effective use of silane-containing adhesives, thus hindering the formation of chemical bonds between the restoration and substrate [5–7]. Several techniques are currently used to overcome the limitations of zirconia modifications such as surface grinding [8,9], airborne particle abrasion (grit-blasting) with Al_2O_3 [10], tribochemical silica coating using SiO_2-coated alumina particles, high concentrated hydrofluoric acid etching (inadequate for clinical use) [11], selective infiltration technique [12,13]. Recently, Electrical Discharge Machining [14] and light irradiation using lasers [15] have been proposed considering significantly changes in roughness and surface topography for mechanical interlocking of veneer materials and resin-matrix cements. Those surface treatments have been complemented with the use of functional monomers-containing primers (e.g. methacryloyloxydecyl didydrogen phosphate – MDP, phosphoric acid acrylate, anhydride, others), to establish a chemical bond to zirconia [5,16]. The combination of alumina grit-blasting, the tribochemical silica coating, and the application of silane and MDP adhesive monomers has increased the bond strength between zirconia and resin-matrix cements [5,6,16]. Nevertheless, the main modification of zirconia surfaces by grit-blasting has limitations to control morphological aspects for mechanical interlocking of the resin-matrix cement.

Several laser irradiation methods have been developed for modifying surface topography of prosthetic structures and improve the mechanical interlocking of the resin-matrix cement. Thus, laser-texturing methods allow the control and reproducibility of surface topography patterns once the parameters are adjusted to each material and application. Previous studies have reported the use of several types of lasers for improving the zirconia adhesion to resin-matrix cements: Nd:YAG [17], Er:YAG [18] , CO_2 [19], Er, Cr:YSGG [20] and Nd:YVO_4 [15]. Nd:YAG lasers working short pulses (nanosecond level) have been referred to be able to increase the bond strength between zirconia and resin-matrix cements [21] although cracks on the surfaces and high monolithic ceramic content can be seen as detrimental to the mechanical performance of the prosthetic structures under fatigue loading conditions [22]. Laser methods with shorter pulses should be the solution to remove small amounts of material without damaging the adjacent surfaces. Ultra-short pulsed lasers (pico- and femtosecond lasers) have been used in different studies with promising results [15,23]. They are able to ablate materials at their very thin surface layers, producing almost defect-free surfaces (without excessive heating and microcracks), although at a very high cost when compared to nano-second laser sources. A possible approach to produce controlled surface morphologies without significant defects while using affordable laser sources (nanosecond pulsed laser) is to irradiate zirconia substrates in their green state (prior to sintering). Monaco et al [24] and Moon et al [22] et al have grit-blasted the zirconia surfaces in the green state while Aras et al [20] laser structured the zirconia surface in a green state. They reported the absence or a significant decrease in cracks alongside with an increase in the amount of tetragonal phase after sintering.

Therefore, the aim of this study was to assess the effect of the laser structuring over zirconia green compacts using a nanosecond Nd:YAG laser (1064 nm) on the adhesion of sintered zirconia to resin-matrix cements. The null hypothesis was that the tensile bond strength of the laser-structured zirconia would not significantly differ from the conventional airborne particle abraded zirconia.

2. Materials and Methods

2.1. Preparation of specimens

In this study a commercial 3 mol% yttria-stabilized zirconia powder TZ-3YBE (Tosoh, Japan) of 6.05 g/cm³ density and 99% purity was used. The zirconia powder was spray dried with the agglomerates size ranging from 20 up to 120 µm and an average size of 60 µm.

Sixty zirconia green compacts (N = 60) with 6 mm height and 10 mm diameter were manufactured by pressing the zirconia powders in a stainless-steel die at 200 MPa for 15 s. The discs were divided into six groups (*n* = 10) according to the type of surface modification. The grit-blasted group (hereafter mentioned as GB) was considered as the control group. Before airborne particle abrasion, the specimens were sintered to full densification (>99%) in a furnace (Zirconofen 700 Vakuum), in air for 2 h at 1500ºC and at a heating rate of 8° C/min. The grit-blasting treatment was performed with 149 µm alumina particles (Al_2O_3) for 30s, at a constant pressure of 6 bar and at a distance of 10 mm from the surface. The final dimensions of the sintered discs were 5 mm height and 8 mm diameter. The specimens of the remaining five test groups were surface textured using a Nd-YAG laser (OEM Plus 6 W, Italy) with 1064 nm wavelength and 20kHz repetition rate. The texturing strategy, consisting in scanning different number (8 or 16) of crossed lines over the surface, are shown in Table 1 and Figure 1.

The laser-textured specimens are referred according to the texturing strategy applied to their surfaces as follows for the G8L group: G stands for Group and 8L stands for the number of lines (i.e. 8 Lines). It must be highlighted at this point that laser texturing was performed while the specimens were in a green state, i.e. after compaction and prior to sintering (Figure 1). After laser texturing, the same sintering conditions previously described for GB specimens were applied. The group G8L/GB was produced in the same way as the group G8L but received a post grit-blasting treatment similar to that previously described for the GB group.

Table 1 – Laser surface structuring parameters used in the different groups.					
Groups	**Scanning speed (mm/s)**	**f (Hz)**	**Number of lines (per 50 µm of linear distance)**	**Number of scans**	**Grit blasted after sintering**
G8L	200	550	8	1	No
G16L	200	550	16	1	No
G8L/GB	200	550	8	1	Yes

After the surface modification of the zirconia disks, the specimens for tensile bond strength tests (set up is shown in Figure 1) were prepared by cementing, with a resin-matrix cement, two zirconia discs with the same type of surface treatment. Prior to the cementation procedure, all discs were ultrasonically cleaned in isopropyl alcohol using a sonicator (Up 200 St Hielscher, Germany) at 100W for 5 s. Then, the adhesive (Ambar, FGM, Joinville, Brazil) was applied to the clean and dry zirconia surface for 20 s according to the manufacturer's instructions. Afterwards, the dual cure resin-matrix cement (Allcem, FGM, Joinville, Brazil) was applied to the surface of the two discs with the same surface treatment. The chemical composition of the adhesive and the resin-matrix cement is shown in Table 2. Specimens were then pressed one against another under a load of 1000 g for 15 min for chemical curing. The remaining excess of resin-matrix cement was gently removed from the specimens' edges using a sharp hand scaler. Specimens were light-cured using Coltolux 75 (Coltène/Whaledent, Altstatten, Switzerland) curing device at 1000 mW/cm^2 for 40 s on each surface. One hour after preparation, the bonded specimens were immersed in water at 37ºC for 24 h.

Table 2. Chemical composition of the adhesive and resin-matrix cement.

Material	Organic matrix	Inorganic fillers
Primer & bond adhesive	Hydrophilic and acid methacrylated monomers, UDMA, HEMA, 10-MDP, camphorquinone, ethyl-4-dimethylaminobenzoate (4-EDAMB), ethanol, water, stabilizers	Silane-treated silica nano-particles
Resin-matrix cement	BISGMA, BISEMA, TEDGMA, camphorquinone, co- initiators	58% wt. silane-treated glass particles of silanized barium-aluminum-silicate, and silica

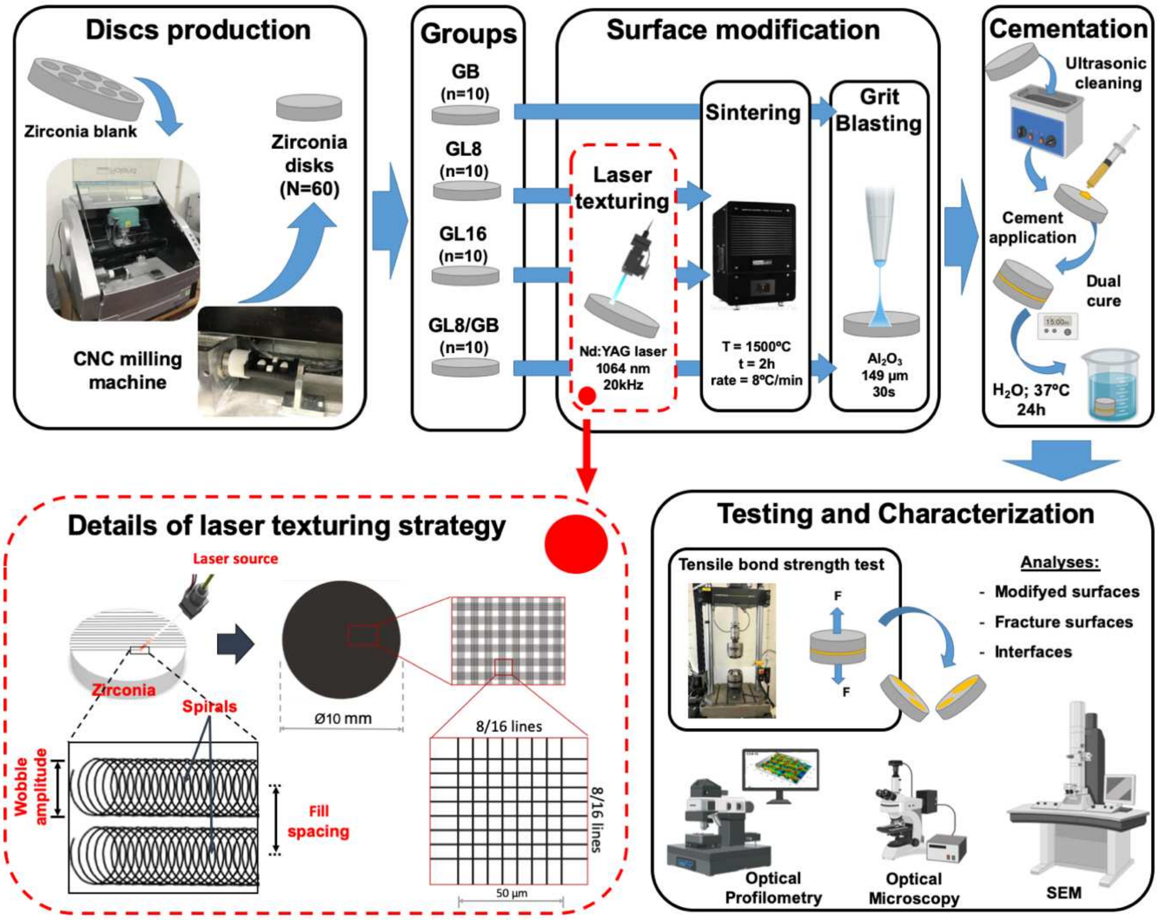

Figure 1 – Schematic of the experimental procedure used in this study: discs production, different groups, types of surface modifications, cementation protocol, and testing and characterization methods. The details of the laser texturing strategy are also provided.

2.3. Microscopic analyses of surfaces and interfaces

The modified surfaces, zirconia-cement interfaces (cross-sectioned specimens) and the fracture surfaces after the adhesion tests were sputter-coated with AuPd thin films and analyzed by Scanning Electron Microscopy (JEOL JSM-6010LV, JEOL GmbH, Freising, Germany). For the analyses of the zirconia-cement interfaces, specimens were cross sectioned at a perpendicular plane to the interface using a diamond disc coupled to precision cutting machine and then wet-ground on SiC papers down to 2000 grit.

2.4. Topographic analyses

For topographic analyses, a white light interferometer (WLI) Profilm3D (Filmetrics, USA), which measures surface profiles and roughness up to 0.05 µm, was used. The analyses were performed using the following parameters: x10 lens, x4 zoom, 300 µm scan length, and 300 µm back scan. A total of three independent scan lines were carried out for each specimen and then post-processed with 25 threshold and 5 pixel region size. The software Mountains Map was used to process the surface topographic data.

2.5. Tensile bond strength tests

The bond strength resulting from each type of modified zirconia surface to the resin-matrix cement was assessed by tensile bond strength tests, as illustrated in Figure 1. Tensile tests were carried out on a universal test machine (Instron 8874, MA, EUA) and the specimens were tested at a speed of 1 mm/min until the maximum fracture/debonding load (N). The tensile bond strength (MPa) was computed as the maximum fracture load (N) divided by the cross-sectional area (mm^2).

2.6. Statistical analysis

The results were analyzed using one-way ANOVA followed by Tukey HSD multiple comparison test. The Shapiro-Wilk test was first applied to test the assumption of normality. P values lower than 0.05 were considered statistically significant.

3. Results

3.1. Morphological and microstructural characterization

The morphologic aspects of the zirconia surfaces of the different groups are shown in Figure 2. The stochastic roughness of the grit-blasted group (GB) contrasts with the patterned structures produced by the laser-textured groups (G8L, G16L and G8L/GB). The morphological details of each type of surface obtained by optical profilometry are shown in Figure 3 and Table 2, where the surface texture is expressed as a combination of waviness (macro-roughness) and roughness (nano and micro-roughness). Waviness is the surface irregularities of longer wavelengths resultant from material removal by the laser action, at the macro-scale. Roughness is produced by fluctuations of short wavelengths characterized by asperities (local maxima) and valleys (local minima) of varying amplitudes and spacing, at the micro- and nanometric scale.

The control group (GB) presented the typical aspect of a grit-blasted surface with peaks and valleys randomly spread over the surface (Figure 2a) and exhibiting an average roughness (Ra) of 0.2 μm. On the other hand, the laser-textured surfaces revealed patterned structures that are different in shape and spatial arrangement. The G8L and G8L/GB groups exhibited dome-like shape (Figures 2b and 2d) while the G16L group exhibited a ridge-shape with flat surfaces on their top (Figure 2c). The orthogonal distance between two consecutive structures (ridge or valley), characterizing the patterning distance, was at 100 μm for surfaces within the G8L group while surfaces of the G16L samples was at 200 μm. Similar height and depths of the surface structures were obtained (~25 μm) since the same laser power and number of scan was used for both groups. The grit-blasting procedure promoted a decrease in the height and depth of those surface structures. The G8L exhibited the highest roughness mean values (Ra=2.49 μm) while G16L and G8L/GB specimens showed lower roughness mean values at 1.34 μm and 1.26 μm, respectively.

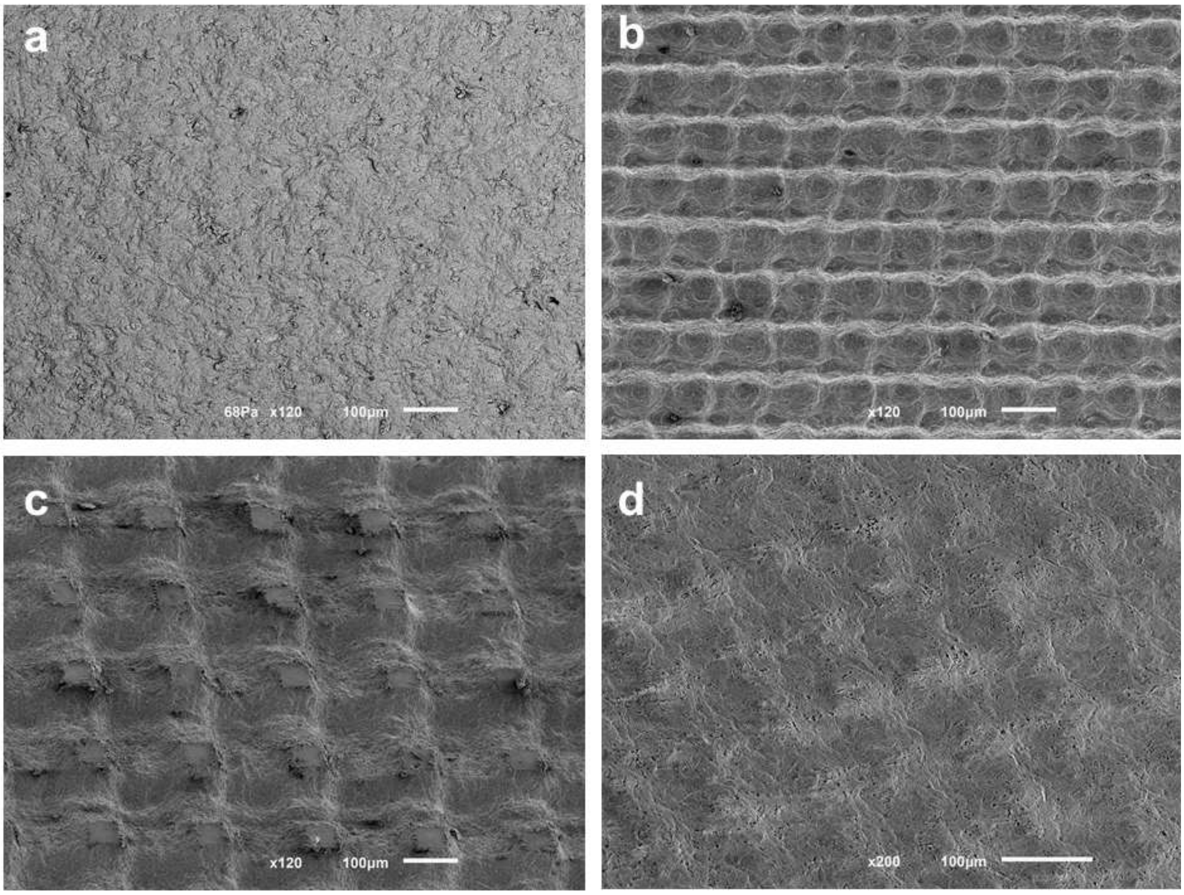

Figure 2 – SEM images of the zirconia surfaces after the different surface treatments: a) GB group with magnification at x120, b) G8L group with magnification at x120. c) G16L group with magnification at x120, d) G8L/GB group with magnification at x200.

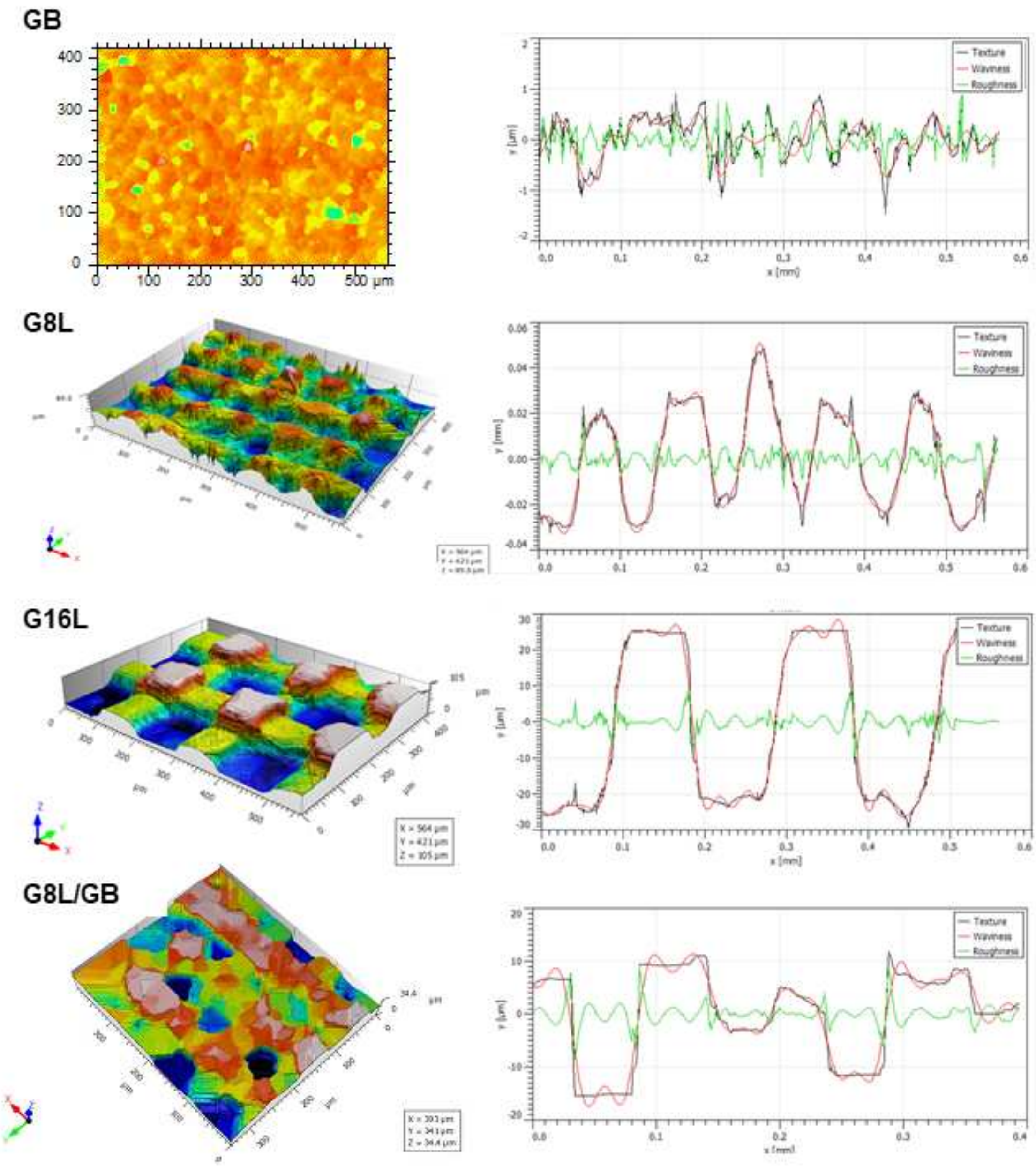

Figure 3 – Surface topographical details of the different surfaces used in this study. On the left side, the representative 3D surface profilometer images. On the right side: texture, waviness, and roughness in selected planes.

Table 2 – Surface topographical parameters of the different groups.				
Groups	Grooves width (µm)	Grooves distance (µm)	Average roughness, Ra (µm)	Waviness average (µm)
GB	n.a.	n.a.	0.20	2.22
G8L	50	100	2.49	19.17
G16L	100	200	1.34	21.09
G8L/GB	50	100	1.26	6.91

3.2. Zirconia to resin-matrix cement interface analysis

The cross-sectional view of the zirconia-cement interfaces obtained for the samples with different surface modifications is shown in Figure 4. The resin-matrix cement appeared in the micrographs as the darker phase layer (GB – Figure 4a; G8L- Figures 4c, G16L-4d and G8L/GB-4e). Also, no significant flaws were noticed in the interfaces, especially in the laser-textured groups, evidencing that the resin-matrix cement was able to successfully flow into the surface irregularities.

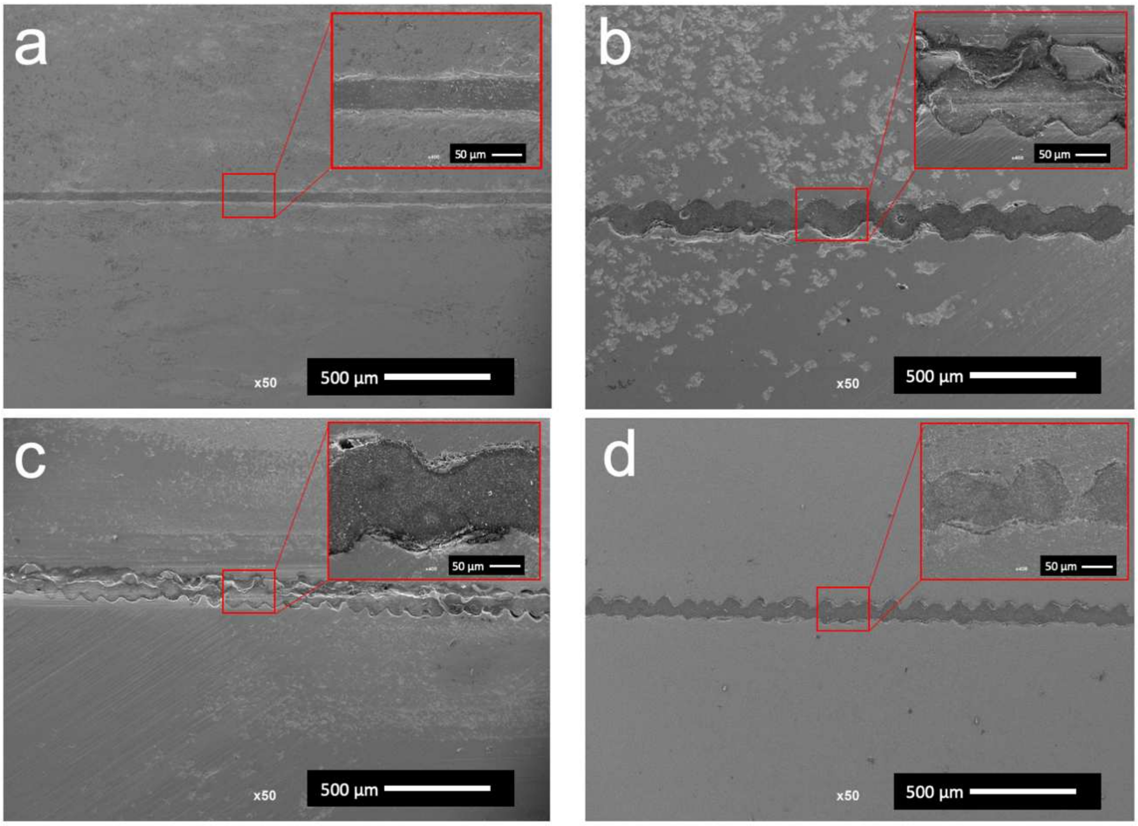

Figure 4 - SEM micrographs showing the cross-sectional view of cemented specimens. Major pictures are displayed at a magnification of x50 and insets at x400 are shows for detailed examination. a) Grit blasted group (GB); b) Laser textured surface – 8 lines – group (G8L); c) Laser textured surface – 16 lines – group (G16L); d) Laser textured surface – 8 lines – and grit blasted group (G8L/GB).

3.3. Tensile bond strength

The tensile bond strength results recorded for the different groups used in this work are shown in Figure 5. The grit-blasted group (GB), showed the lowest bond strength values (10.0 ±3.1 MPa) while the laser-structured surfaces G8L and G16L yield higher bond strength results, 16.7 ±3.8 MPa and 13.6±3.0 MPa, respectively. The G8L/GB group, which combined the laser structuring and grit blasting treatment, exhibited the highest tensile bond strength values (24.2 ±7.6 MPa) ($p<0.05$).

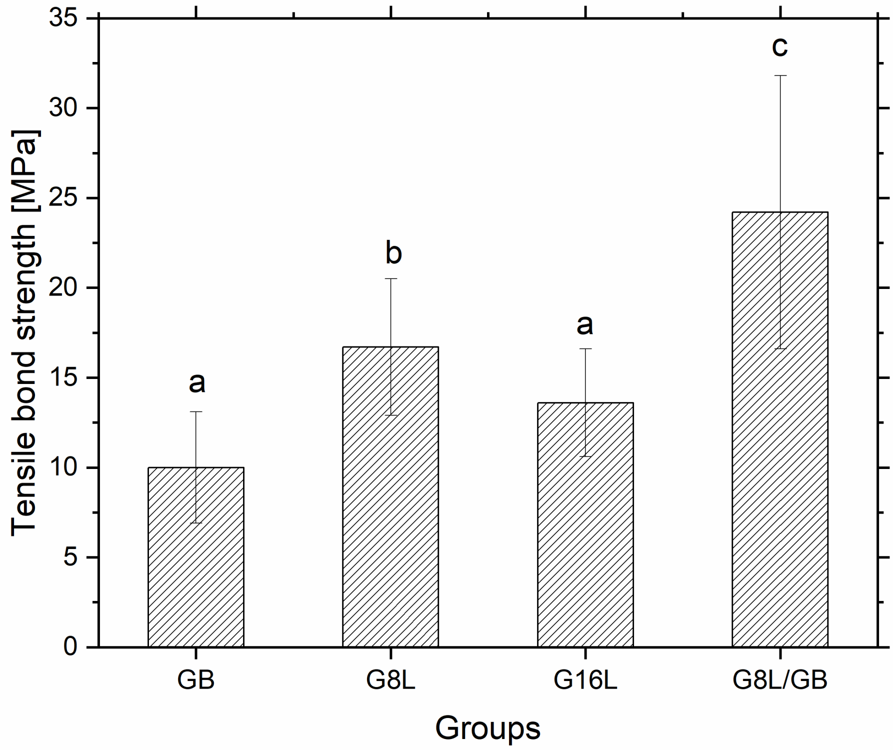

Figure 5 – Tensile bond strength results of the modified zirconia surfaces to the resin-matrix cement. Different letters indicate statistically significant differences within the groups ($p < 0.05$).

3.4. Fracture surface analysis

SEM images of the fracture surface of the test specimens are shown in Figure 6. The grit-blasted specimens (GB) revealed typically a mixed fracture, with a few remnants of resin-matrix cement being visible at the surface (noted as the darker phase in Fig. 6a). Figures 6b and 6c, shows the micrographs of two particular cases occurring in the laser structured groups, where it is possible to see the full infiltration of the resin-matrix cement into the structured surfaces, thus creating a strong interlocking that lead the rupture to occur throughout the structured parts of the surface (at the base of the ridges). At the same time, it can also be seen in these specimens the fracture taking place at the base of the ridges and pillars. This phenomenon is further addressed in the discussion section and it was attributed to the defects/cracks generated by the laser structuring process. The fracture surface of G8L/GB specimens showed a mixed surface fracture with significant amount of remaining cement over the surface and without signs of fractured zirconia structures. Such findings are in accordance with the highest bond strength values obtained. The post-blasting treatment after laser structuring is pointed as the responsible for this effect.

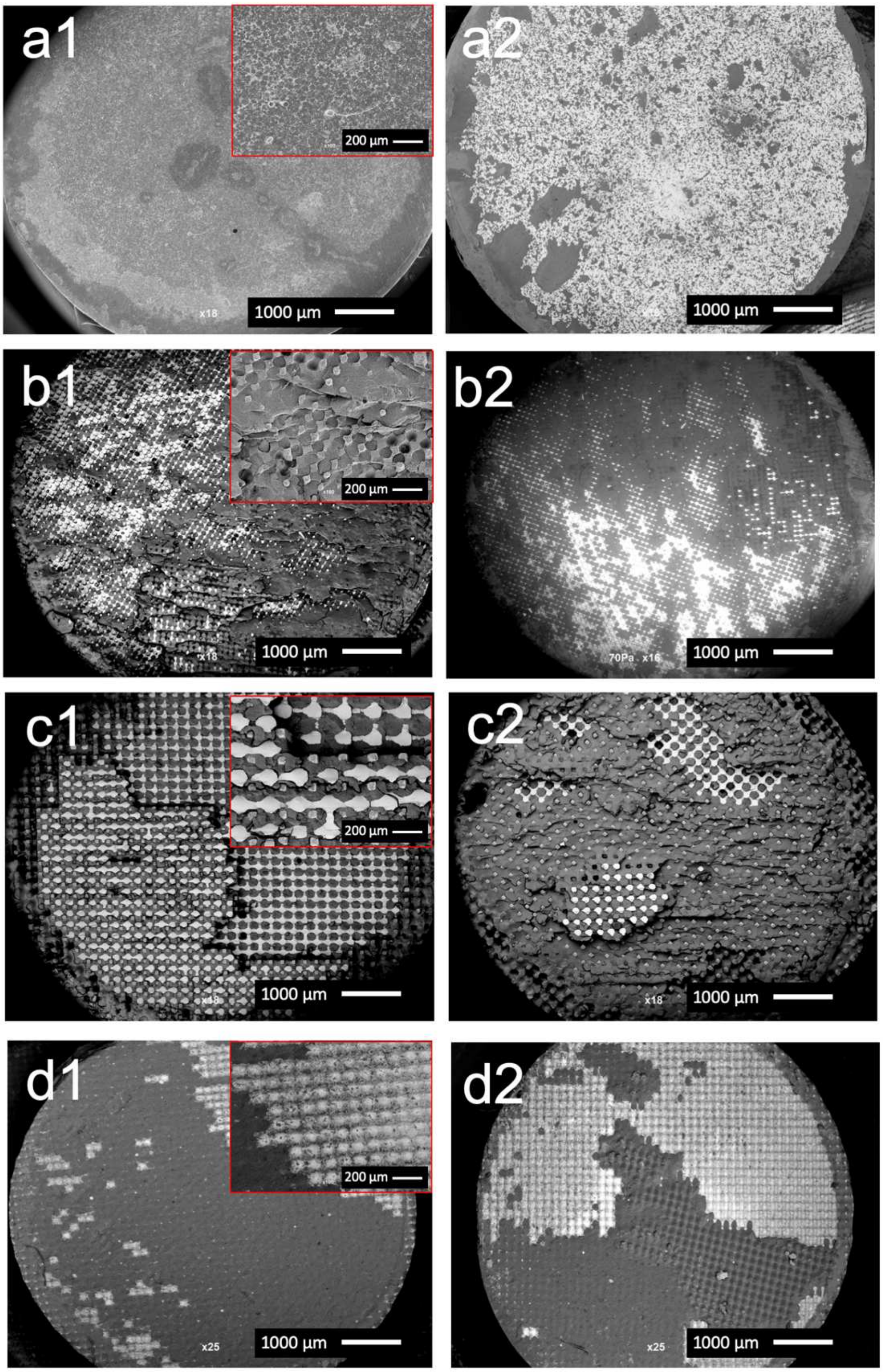

Figure 6 – SEM micrographs of the typical fracture surfaces of the different groups (the two faying surfaces are shown for each specimen). Higher magnification insets are also shown. a1,a2) Grit-blasted group (GB); b1,b2) Laser-textured surface – 8 lines – group (G8L); c1, c2) Laser-textured surface – 16 lines – group (G16L); d1,d2) Laser-textured surface – 8 lines – and grit-blasted group (G8L/GB).

As seen in Figure 7, the relationship between the fracture type and the adhesion was evaluated and therefore the amount (%) of remnant resin-matrix cement left on the zirconia substrates were plotted against the tensile bond strength mean values of each zirconia to resin-matrix cement specimen in this study. It can be seen that in the case of laser-structured specimens (Figure 7b, 7c and 7d), higher bond strength values were associated to higher percentage of remnant resin-matrix cements on the surface while lower bond strength values typically yield lower remnant percentages of resin-matrix cement. On the other hand, no such correlation for the case of the grit-blasted specimens was noticed (Figure 7a).

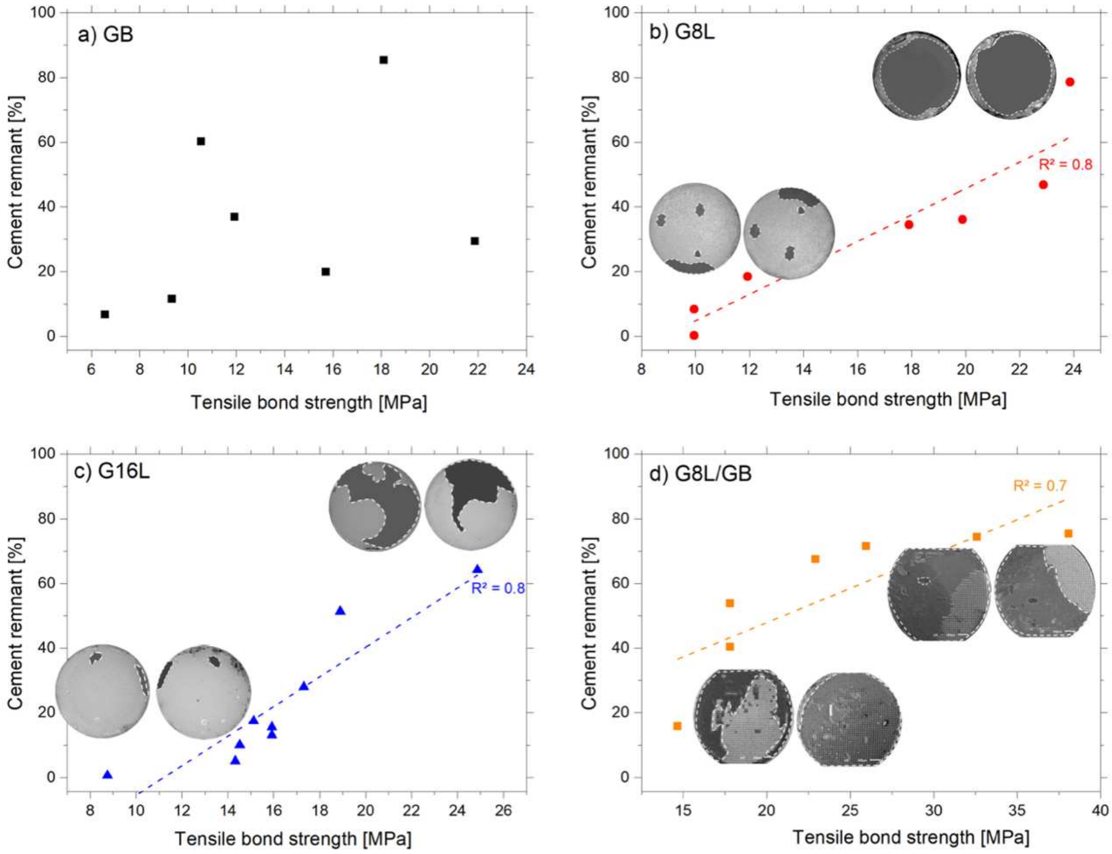

Figure 7 – Graphs plotting the relationship between the amount (%) of remnant resin-matrix cement left over the fracture surface after tensile bond strength tests and the corresponding tensile bond strength values measured for each specimen. A correlation between the adhesion strength and the cement remnant could be noticed for laser-textured specimens: b) G8L, c) G16L and d) G8L/GB. The two fracture surfaces of a representative specimen of each group, for the conditions of low and high bond strength, are embedded in the respective graphs.

4. Discussion

The null hypothesis of this study was rejected, as the laser textured zirconia surfaces revealed significantly higher bond strength to resin cement than that recorded for conventionally alumina blasted ones ($p<0.05$). The laser conditions used in this work were selected based on previous experiments in a way that surfaces with different pattern arrangement could be produced in a controlled manner (Figure 2b-d) [25]. The surfaces produced consisted of equally spaced valleys and protrusions, being closer in the G8L samples and further apart in the G16L samples. This type of morphology conduces to higher surface area and consequently higher bonding area. In addition to the different patterns, the different laser scanning strategies also conducted to different surface roughness, which was slightly higher in the G8L (Ra = 2.49 μm) than within the G16L (Ra = 1.34 μm) group specimens. The increase in roughness promote a proper wettability of the adhesive and also provide a mechanical interlocking between the zirconia substrate and the resin-matrix cement, which should be coupled to a wider contact area for improved adhesion or osseointegration of implants [15,17,26,27].

Several types of lasers using different wavelengths and processing parameters have been used for laser texturing zirconia surfaces with the aim of improving adhesion to resin-matrix cements. The findings pointed out generally to improved bond strengths over ordinary grit-blasting treatments [15], but opposite behavior was also reported [20]. However, such data must be carefully analyzed as different lasers and processing parameters may conduce to different surface morphologic aspects, which in turn govern the adhesion pathways. One very important issue is the laser pulse time, as shorter pulsed lasers tend to be less harmful to the working surfaces, producing nearly, if not entirely defect-free surfaces [23,26,27]. Nanosecond pulsed lasers, similar to that used in this study, have been referred as not to be the most appropriate to texture zirconia surfaces due to the significant level of microcracks left at the surface [21]. Nevertheless, ns-Nd:YAG lasers are among the mostly used lasers today and, for this reason, an alternative based on laser-texturing the zirconia surface in its green state (pre-sintered) has been proposed in our study aiming at overcoming these limitations. Such approach has also been reported in previous studies to avoid the thermal-based surface damage and also the tetragonal to monoclinic phase transformation often seen in laser textured zirconia dense parts [17], since the post high temperature sintering step can restore the totality of the tetragonal phase to the entire zirconia part [22].

The tensile bond strength results of this study showed improved adhesion of laser-structured surfaces over the ordinary alumina blasted surfaces (10.0 ±3.1 MPa). Hence, the G8L group specimens (16.7 ±3.8 MPa) exhibited enhanced bond strength relative to G16L group (13.6 ±3.0MPa) and these results seem to be related to the higher bonding area exhibited by the former specimens. The highest bond strength was however registered for G8L/GB specimens (24.2 ±7.6 MPa), which consisted in G8L group specimens that had undergone a grit-blasting post-treatment. The bond strength mean values reported in literature for macro-tensile test is approximately 23 MPa [16,28], which is in the range of the maximum values recorded in our study. However, the results of the present study must be analyzed within the frame of the physical treatment for surface morphologic modifications free of chemical modification of the zirconia surfaces (e.g. silica coating). Such behavior was somehow expected and that is in agreement with the findings reported in a previous study of Inokoshi et al. [28] in which lower bond strength results were recorded for zirconia free of mechanical or chemical treatment than for laser-irradiated zirconia but not chemically pre-treated.

The analysis of the fracture surfaces supported the bond strength results (Figure 6). Thus, fracture took place on the resin-matrix cement at the base of the ridge of the surfaces for G8L and G16L group specimens due to the higher bond strength caused by a full infiltration of the resin-matrix cement in the laser-texturized surfaces. The analysis of the fracture surfaces for the GL8/GB group (Figure 6) did not reveal signs of such type of fracture. In fact, the grit-blasting treatment removed any cracked/defected asperity or structure that could act as a crack initiation site, which could in turn weaken the interface to the resin-matrix cement. This is also seen in the surface waviness reduction of the G8L/GB group specimens (6.91 µm) as compared to the G8L (19.17 µm), as seen in Figure 2 and Table 2. Additionally, the grit-blasting treatment also promoted the formation of residual compressive stresses at the zirconia structured surface [29], which seems to strength the blasted surfaces structures and hinder their fracture when pulled out by the resin-matrix cement.

The analysis of the correlation of the fracture type together with the tensile bond strength results also revealed interesting findings. The specimens of each group were arranged from the lowest to the highest bond strength values and the corresponding percentage of remnant resin-matrix cement was registered and plotted in the same graph, as shown in Figure 7. A correlation between the bond strength and the remnant cement could then be carefully evaluated for laser-treated specimens, once the higher and lower bond strength values exhibited higher and lower percentage of remnant cements over the surfaces, respectively. The higher bond strength values were characterized by high amount of remnant resin-matrix cement over the surface and therefore by a cohesive fracture type of the resin-matrix cement, since the bond strength of the joint was limited by the strength of the resin-matrix cement, as ideally should be. On the other hand, the grit-blasted (GB) specimens showed scattered data and no such correlation could be established.

Several different bond strength set up configurations have been reported in literature to assess the bond strength of ceramic to resin-matrix cements, although there is no currently standard method that allow a common protocol to compare the different studies [16,30] . The most commonly used tests have been the tensile- and the shear-tests at micro- or macro-scale depending on the specimens' dimensions. Despite the shear bond strength tests have been more extensively used due to the simplification of samples' preparation and test apparatus, strong criticism are reported on the results recorded by shear tests [16,30]. Shear bond strength tests are characterized by a non-uniform stress pattern that induce cohesive failures of the substrate, which tends to give information on the strength of the base material rather than the bond [30]. The tensile bond strength tests have been also used, although in a smaller extent, mainly due to the higher complexity of the test set up and specimens' preparation. Nevertheless, the test has been pointed out as the most suitable test for the adhesion evaluation of ceramic to resin-matrix cements [30] and therefore has been selected for this study.

Physical techniques based on airborne particles abrasion followed by the use of silica-coated particles to provide the chemical surface modification, have been reported in literature as to an effective approach to improve the adhesion between zirconia and resin-matrix cement [6,16,31]. Considering additional chemical bonding between zirconia and methacrylate-based adhesive and resin-matrix cements, trimethoxysilyl-propyl methacrylate (MPS) silanes and 10-methacryloxydecyl dihydrogen phosphate (10-MDP) are monomers which are associated with high bond strength values [32]. In literature, the highest bond strength values are reported for zirconia subjected to tribochemical silica in combination with MPS silane coatings or for alumina-blasted zirconia coated with MDP monomers [33]. Regarding previous findings, MDP-containing adhesive and resin-matrix cements have been used in our study to assure the synergistic effect of the chemical pathways for improved bond strength. Although zirconia has well-known optical and mechanical properties, the surface modification and adhesion of zirconia to resin-matrix cement are still current clinical limitations. More recently, zirconia surface conditioning using different lasers and patterning strategies has also been reported [15,17–20,23]. The synergistic effect of combined ordinary physical, chemical, and advanced laser-structuring methods would improve the adhesion of zirconia to resin-matrix cements. However, the improvement of the interface might be limited by the properties of adhesives and resin-matrix cements that should also be the focus of further studies.

5. Conclusions

In this work, the laser-texturing of zirconia green compacts using a ns-Nd:YAG laser (1064 nm) has been assessed as an alternative technique to the ordinary alumina grit-blasting of zirconia surfaces for improving the adhesion strength to resin-matrix cements. Based on the results, the following conclusions could be drawn:

- Controlled laser patterned surfaces were successfully produced in green (unsintered) zirconia compacts. The crack-like defects were prevented by using a laser-structuring approach prior to the thermal treatment (sintering) of the zirconia parts;
- Laser-structured surfaces with different patterns (G8L and G16L) showed higher tensile bond strength values of zirconia to resin-matrix cements (16.7 ±3.8 MPa for G8L and 13.6 ±3.0MPa for G16L) as compared to ordinary alumina blasted surfaces (GB: 10.0±3.1 MPa). The highest tensile bond strength results were recorded for laser-textured zirconia surfaces followed by additional alumina blasting treatment (24.2 ±7.6 MPa for G8L/GB);
- The mixed type of fracture was mostly present in all groups after the tensile bond strength tests. A correlation between the bond strength results and the percentage of remnant resin-matrix cement over the surface of laser-treated zirconia was observed.
- In fact, the synergistic effect of combined ordinary physical, chemical, and advanced laser-structuring methods would improve the adhesion of zirconia to resin-matrix cements. However, the improvement of the interface might be limited by the properties of resin-matrix cement that should also be the focus of further studies. Currently, there is a need for developing novel adhesives and resin-matrix cements with improved strength and long-term mechanical stability in the aggressive oral environment.

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